DYNAMIC STUDIES OF THE INTERACTION OF IRON SULFIDES WITH HYDROGEN

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ABSTRACT

Controlled atmosphere electron microscopy and in-situ electron diffraction techniques have been used to study the manner by which various iron sulfides interact with hydrogen using graphite as a probe material. When the metal sulfide was in direct contact or physically separated from the graphite probe, pitting of the basal plane regions was observed even at room temperature. This unusual behavior is believed to result from the action of atomic hydrogen on the metal sulfide particles. These species are extremely reactive towards the π-electrons present on the graphite basal planes and this action leads to the creation of pits. At the low pressures used in this work, 0.2 Torr, it is clear that the atomic species can migrate not only by surface diffusion processes (spillover) but also by transport through the gas phase.

INTRODUCTION

The notion of using atomic hydrogen to convert carbonaceous solids to a variety of hydrocarbon products has been the subject of a number of investigations[1-10.] This type of study has also been extended to cover the interaction of atomic hydrogen with various coals [6-10]. Sanada and Berkowitz [6] compared the reactivity pattern arising from the interaction of atomic hydrogen with various coals to that with graphite. They found that a complex mixture of gaseous hydrocarbons was produced from the coal samples, whereas when graphite was the reactant methane was the sole product. Amano and coworkers [7,8] carried out a very comprehensive examination of the products generated from the interaction of a Japanese subbituminous coal with atomic hydrogen at 200°C and reported that gaseous hydrocarbons accounted for only 10 to 15% of the coal converted, the major product being a liquid which consisted of C_5 to C_{22} alkanes and cycloalkanes. A somewhat different product spectrum was found by Wong and coworkers [9] from their investigation of the reaction of atomic hydrogen with a bituminous coal (Illinois No 6), where the major products were low molecular weight volatile hydrocarbons (methane, acetylene, ethylene and propane).

Transition metal sulfides are used extensively as hydrotreating catalysts with the most important reaction in this category been hydrodesulfurization (HDS) and there are a number of excellent reviews on this subject [11-14]. In such systems the precise manner by which hydrogen interacts with the sulfide catalyst is a key factor to the understanding of the mechanism. Wright and coworkers [15] studied the interaction of hydrogen with alumina supported molybdenum disulfide catalysts using a combination of hydrogen adsorption and inelastic neutron scattering techniques. They found that

the uptake of hydrogen was several times higher than that which was expected from nitrogen adsorption experiments. In order to account for this unusual behavior they suggested that the adsorption of extra hydrogen could arise from intercalation into the layered structure of the sulfide particles or alternatively as a result of hydrogen "spillover" onto the alumina support.

In the current investigation we have attempted to gain a clearer understanding of the manner by which hydrogen interacts with various iron sulfides as a function of temperature by using controlled atmosphere electron microscopy techniques. In these experiments graphite has been used a a probe material since its reactivity in both molecular and atomic hydrogen is well characterized

EXPERIMENTAL

The experiments reported here were carried out in a modified JEOL 200CX TEM electron microscope, which allows one to continuously observe the behavior of a specimen as it is heated in the presence of a gas environment. In addition to being able to directly follow changes in the appearance of a specimen as it is undergoing reaction it is also possible to use the microscope in the diffraction mode and obtain information about the chemical state of the specimen at any stage of the experiment.

In this investigation two types of specimen arrangements were utilized. (a) The catalyst particles (metal sulfide) were placed in direct contact with the graphite specimen, and the observations made were limited to areas in the vicinity of the catalyst particles. (b) A microscope grid was cut in half and one section contained a pristine transmission graphite specimen and on the other, the catalyst mounted in the same manner as shown in (a). In this arrangement the catalyst and graphite probe reactant were physically separated. It was essential that when this type of specimen was placed into the environmental cell the reactant gas stream came into contact with the catalyst prior to passing over the clean graphite, the component under observation.

RESULTS AND DISCUSION

(a) Iron Sulfide/Graphite-Hydrogen

When graphite specimens containing particulates of either FeS2 or FeS were exposed to 0.2 Torr hydrogen a very unusual pattern of behavior was observed. Immediately following the introduction of the gas attack of the basal plane regions of the graphite support took place at room temperature. This action initially took the form of the creation of very tiny pits which became visible when their width had expanded to approximately 1.2 nm and their depths reached a level sufficient to allow a contrast difference to be observed in the transmission image between the pit and the surrounding unattacked graphite.

It was evident that in the early stages of the reaction the pits tended to be generated in clusters which were aligned in definite directions with respect to the graphite substrate. Examination of numerous areas showed that the hexagonal arrangement was predominant. On continued reaction at the same temperature the pits increased in size and in a given group gradually merged with each other to form a single larger entity up to 10 nm in width. Examination of these more highly developed pits showed

that they tended to acquire a hexagonal outline and a this stage generally contained an internal region of unattacked carbon.

The intensity of the reaction increased significantly as the temperature was gradually raised to 200°C. Unfortunately, the indiscriminate mode of attack made it impossible to identify any dynamic events that could be followed for the purposes of estimating rates of graphite hydrogenation. Moreover, the gradual deterioration in quality in the transmission image due to collection of deposit on the specimen made it difficult to resolve many surface features. In studies where the temperature was held at 350°C for extended periods of time the attack became so extensive that specimens lost their integrity and experiments were normally terminated.

On continued heating to above 500°C, the sulfide particles were observed to exhibit a change in morphological characteristics from faceted structures to a more globular geometry. This transformation which occurred at about 725°C with the iron sulfides was most clearly evident with particles located at edge regions which appeared to be quite fluid and tended to wet the graphite. This behavior was a prelude to the restoration of catalytic activity, seen as the propagation of channels by these particles when the temperature was increased by a further 100°C.

A more fundamental understanding of the factors which control the ability of a supported particle to undergo morphological changes can be obtained from a treatment of the surface forces operative at the particle-support-gas interface. Consider the situation of a metal sulfide particle located at the edge site of a carbonaceous solid exposed to a hydrogen environment, as depicted in Figure 1. The contact angle, θ at equilibrium is determined by the surface energy of the support, γ_{GS}, the surface energy of the metal sulfide particle, γ_{PG}, and the particle-support interfacial energy, γ_{PS}, and is expressed in terms of Young's equation:

$$\gamma_{GS} = \gamma_{PS} + \gamma_{PG} \cos \theta \qquad \{1\}$$

or
$$\cos \theta = \frac{\gamma_{GS} - \gamma_{PS}}{\gamma_{PG}} \qquad \{2\}$$

If γ_{PG} is larger than γ_{GS}, the contact angle is greater than 90° and the particle is in a non-wetting state, if the reverse is true, θ is less than 90°, then wetting occurs, and if $\gamma_{GS} = \gamma_{PS} + \gamma_{PG}$, then the particle will spread out over the support surface in the form of a thin film. Spreading of the catalyst particle results in the most efficient use of the additive in that the contact area between catalyst and carbon atoms is maximized.

The ability for particles to undergo the morphological transformations mentioned above indicates that a significant degree of atomic mobility exists, particularly in the surface layers. Previous studies [16], have demonstrated that this phenomenon can occur below the Tammann temperature of the material constituting the particles, which is calculated from 0.52 [bulk melting point {K}]. For iron sulfides the Tammann temperature is about 480°C, and for systems such as those studied in this work, where a weak interaction exists with the support, particles will exhibit mobility at this temperature [17].

In an attempt to determine whether the catalytic action could be sustained at even greater distances from the sulfide particles, another set of experiments was carried out

using a different specimen design. This involved complete physical separation of the supported metal sulfide and the graphite probe component. When this combination was treated in 0.2 Torr hydrogen then attack of the unadulterated graphite surface was once again observed at room temperature. In these systems, however, there was a modulation in the severity of the reaction compared to that where the catalyst and graphite were in intimate contact. It was significant to find that the incidence of pit formation showed a steady decline as one scanned across the graphite surface in the opposite direction to that where the sulfide catalyst particles were located.

A feature which must always be taken into consideration with experiments carried out within the electron microscope is whether the electron beam exerts any effect on either the gas or the solid under investigation. Concern that this problem was being encountered in the current work was dispelled by performing "blank experiments" in which specimens were reacted in hydrogen with the beam turned off for periods of up to two hours. When such specimens were eventually examined it was clear that there have been extensive reaction prior to exposure to the beam.

(b) In-Situ Electron Diffraction Analysis

In a final series of experiments the electron microscope was operated in the *in-situ* diffraction mode and patterns taken of the FeS_2/graphite specimens at various stages of the reaction during heating from room temperature up to 850°C in 0.2 Torr hydrogen. Examination of the data summarized in Table 1 shows that reduction of FeS_2 to FeS and Fe_7S_8 (Pyrrhotite) starts to occur at 240°C and at 400°C respectively, and these latter sulfides become the stable phases. At 600°C FeS appears to be the only phase present, however, on increasing the temperature to 750°C metallic iron (γ) begins to appear along with Fe_3C.

The major feature which emerges from this study is that the interaction of hydrogen with certain metal sulfides produces a species, which even at room temperature is highly reactive towards the π-electrons present on the graphite basal plane and this action leads to the creation of pits. The observation that the carbonaceous solid does not necessarily have to be in direct contact with the metal sulfide particles in order for hydro-gasification to occur, indicates that at the gas pressure used in these experiments, it is possible for the active species to be transported through the gas phase in addition to the surface migration route. The intensity of this action appears to increase with temperature up to a certain point and then come to a complete halt. Catalytic activity could, however, be regenerated by lowering of the temperature to a previously active regime.

This intriguing pattern of behavior can be rationalized according to the following arguments. At low temperature graphite can only undergo attack due to interaction with atomic species, generated from the dissociation of molecular hydrogen with metal sulfides via a reversible chemisorption process. This reaction will continue until conditions are reached which favor weakening of sulfur-metal bonds and the concomitant release of hydrogen sulfide. At higher temperatures, the sulfides are converted to the metallic state and the mode of gasification of graphite will revert to that normally associated with the metal, i.e. channeling.

ACKNOWLEDGMENTS

REFERENCES

1. Blackwood, J. D., and McTaggart, F.K., Aust. J. Chem., 12, 533 (1959).

2. Gill, P. S., Toomey, R. E., and Moser, H. C., Carbon 5, 43 (1967).

3. Vastola, F. J., Walker, Jr., P. L. and Wightman, J. P., Carbon 1, 11 (1963)

4. Wood, B. J., and Wise, H., J. Phys. Chem, 73, 1348 (1969)

5. McCarroll, B., and McKee, D.W., Carbon, 9, 301 (1971)

6. Sanada, Y., and Berkowitz, N., Fuel, 48, 375 (1969).

7. Amano, A., Yamada, M., Shindo, T., and Akakura, T., Fuel 63, 718 (1984).

8. Amano, A., Yamada, M., Shindo, T., and Akakura, T., Fuel 64, 123 (1985).

9. Wong, C.-L. Chen, C.-W. and Timmons, R. B., Fuel 65, 1483 (1986).

10. Gesser, H. D., and Czubryt, J. J., Fuel 67, 375 (1988).

11. Massoth, F.E., Adv. Catal. 27, 265 (1978).

12. Delmon, B., in Proc. Climax Third Intern. Conf. on Chemistry and uses of Molybdenum (H.F. Barry and P.C.H. Mitchell, eds) Climax Molybdenum Co. Ann Arbor, Michigan 1980, p 73.

13. Grange, P. Catal. Rev. Sci. Eng. 21, 135 (1980).

14. Topsoe, H. and Clausen, B. S., Catal. Rev. Sci. Eng. 26, 395 (1984).

15. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B. and Riekel, C., J.C.S. Faraday I 76, 1585 (1980).

16. Derouane, E.G., Baker, R. T. K., Dumesic, J. A. and Sherwood, R. D., J. Catal. 69, 101 (1981).

17. Baker, R. T. K., J. Catal. 78, 473 (1982).

TABLE 1. IN-SITU ELECTRON DIFFRACTION ANALYSIS OF FeS2 REACTING IN H2

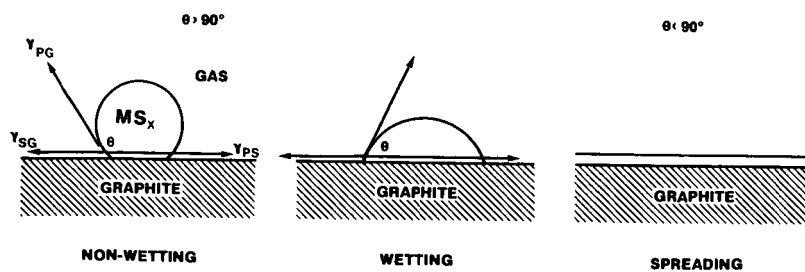| TEMPERATURE (°C)	PHASES PRESENT
240	FeS_2; FeS^*
300	FeS_2; FeS
400	FeS_2; FeS; Fe_7S_8
500	FeS_2; FeS; Fe_7S_8
600	FeS
700	FeS
750	FeS; Fe_3C; $\alpha\text{-}Fe^*$; $\gamma\text{-}Fe$

Figure 1. Metal Sulfide-Graphite-Hydrogen Interaction

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* Possibly present

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